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GTRI

July 27, 1987

Dr. Jim B. Robertson/494
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Dear Jim:

Please find enclosed the six-monthly report due for October 1, 1986 to March 31, 1987. This work has been written up in paper form and will be given as a 20-minute oral presentation at the Third International Conference of II-VI Materials to be held in Monteray, CA, next week. I apologize for the delay in this report and will call you soon to discuss our recent work.

Sincerely,

Chris Summers

Chris J. Summers, Chief
Physical Sciences Division

CJS/al

MOLECULAR BEAM EPITAXIAL GROWTH AND STRUCTURAL CHARACTERIZATION OF ZnS ON (001) GaAs

by

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Abstract

The effect of surface nucleation processes on the quality of ZnS layers grown on (001) GaAs substrates by molecular beam epitaxy is reported. Reflection high energy electron diffraction indicated that nucleation at high temperatures produced more planar surfaces than nucleation at low temperatures, but the crystalline quality as accessed by x-ray double crystal diffractometry is relatively independent of nucleation temperature. A critical factor in layer quality was the initial roughness of the GaAs surfaces.

1. INTRODUCTION

The growth of crystalline ZnS layers on foreign substrates offers the potential to fabricate thin-film electroluminescent devices for flat panel display applications. Silicon is an obvious substrate choice because of its high crystalline quality and close lattice-match with ZnS. Although ZnS epitaxial growth was obtained on silicon using molecular beam epitaxy (MBE) and organometallic vapor phase epitaxy (OMVPE), difficulties in oxide removal and the thermal mismatch between these materials makes it prudent to consider other substrate choices [1-4]. An alternative substrate material, GaAs, has considerable advantages in that its thermal expansion coefficient is well matched to ZnS and the procedures for oxide removal are established. In addition, epitaxial ZnS has been grown on GaAs using both the MBE and OMVPE techniques [5-8]. Processes must be developed, however, to overcome the effect of the ~4.5% mismatch between GaAs and ZnS.

Recent MBE studies of ZnSe and CdTe growth on GaAs found a strong reaction between the thermally-cleaned GaAs surface and the group VI element, resulting in the formation of a As-deficient $GaAs_x(VI)_y$ layer [9,10]. Other studies have reported a reaction between H_2S and the GaAs (001) surface which results in the displacement of arsenic and the formation of a layer of $GaAs_xS_y$ or Ga_2S_3 [11,12]. For low concentrations of sulfur, $GaAs_xS_y$ retains the sphalerite structure but with a smaller lattice constant [13]. Two effects could contribute to ZnS layer improvement if it is grown on a $GaAs_xS_y$ surface. If this surface layer is unstrained, the lattice-mismatch and corresponding misfit dislocation density would be decreased. However, if the surface layer is strained to the GaAs substrate, the lattice-matching effect would be negated, but, the tetragonal distortion and the accompanying change of surface potential in the $GaAs_xS_y$ layer could modify the initial nucleation phase of the ZnS epitaxial layer, favoring two-dimensional growth. The subsequent reduction in three-dimensional island density will minimize stacking fault, twin and dislocation densities in the epitaxial layers.

In the course of the work described below, the interaction between the Zn/S_2 molecular beam and the GaAs (001) surface was studied using reflection high energy electron diffraction (RHEED) and the optimal nucleation temperature of ZnS on GaAs was determined. Epitaxial layers 0.1 - 2.1 μm thick were grown using these procedures and their structural quality was characterized by double crystal rocking curve (DCRC).

2. EXPERIMENTAL PROCEDURES

The ZnS layers were grown in a Varian MBE GEN II equipped with a 10 KV electron gun for RHEED. A single furnace loaded with polycrystalline ZnS provided a flux of atomic zinc and sulfur dimers. All GaAs wafers were misoriented from the (001) direction by 2^{o} towards the nearest (011) plane. The GaAs substrates were prepared for growth by first degreasing in organic solvents, followed by etching in a 5 H_2SO_4 - 1 H_2O_2 - 1 H_2O solution cooled to room temperature. Residual aqueous surface oxides left by the etch were removed using a 1 NH_4OH - 1 H_2O solution. The substrates were then air-baked to insure a reproducible surface oxide before In-mounting.

As a precursor to the surface and growth studies, an oxide-free surface was obtained by slowly heating the substrate to temperatures between $550^{o}C$ and $615^{o}C$. Two nucleation procedures for the ZnS epitaxial layers were investigated. In the high temperature procedure, the Zn and S_2 flux was incident on the GaAs surface at the oxide desorption temperature, after which the substrate was cooled under the flux to the growth temperature (typically 175^{o}). In the low temperature procedure, the substrate was cooled to the growth temperature after oxide desorption at which time the ZnS furnace shutter was opened to initiated growth.

A prototype of the Bede Model 150 double axis diffractometer was used to measure rocking curves. The nondispersive arrangement, the [004] diffraction peaks for both the (001) GaAs monochromator crystal and the ZnS/GaAs sample and Cu Kα radiation from a 0.6 x 1.6 mm^2 spot focus were used. A 1mm collimator was positioned before the monochromator to limit the irradiated area of the specimen to 2mm x 6mm. A limited number of measurements were made with a narrow collimator (approximately 0.25mm diameter) to investigate whether layer inhomogeneity contributed to the observed rocking curve widths. A gonimeter head and translator allowed precise sample alignment and positioning. Diffraction from asymmetric planes (113) and ($\bar{1}\bar{1}3$) was used to investigate whether dislocation density decreased significantly away from the ZnS/GaAs interface.

Misorientation of the layer relative to the substrate, $\Delta\theta$(GaAs,ZnS), $[001]_{ZnS}$ relative to $[001]_{GaAs}$, was determined by measuring the substrate-layer peak separation Ω(GaAs ZnS) as a function of ϕ, the angle between $[110]_{GaAs}$ and the plane of the diffractometer. The true value of $\Delta\theta$ (GaAs, ZnS) was obtained when both the GaAs and ZnS normals lie in the plane of the diffractometer.

3. RESULTS AND DISCUSSION

3.1 Nucleation and Growth Characterization

The RHEED patterns from the GaAs surface after oxide desorption are shown in Fig. 1a and b for two azimuthal orientations. A 4-fold reconstruction was present in the [110] azimuth while the [$1\bar{1}0$] was 6-fold reconstructed. Intensity modulation along the streaks resulted from surface roughness while the presence of chevrons in the [$1\bar{1}0$] azimuth indicated surface facetting [14,15]. Two possible explanations for facetting are carbon contamination of the substrate [16] or the chemical etching procedure [17-19]. The degree of surface roughness depended on both the etching time and the air-bake and In-mounting procedure for the GaAs substrate. Long etch times resulted in increased surface roughness, in agreement with Aspnes et al. [17-19]. Prolong heating of the substrate in the cleanroom atmosphere during air-baking or In-mounting also increased the surface roughness observed in both azimuths. This surface roughness had a major influence on the final quality of the epitaxial layer surface and crystallinity.

The appearance of the RHEED patterns also depended on the vacuum conditions in the growth chamber. Surfaces similiar to those shown in Fig. 1a and b except for varying degrees of surface roughness were routinely obtained after oxide desorption when all source furnaces were idling below 250°C. However, when oxide desorption was performed with the ZnS oven at the deposition temperature (1000°C - 1100°C), the RHEED patterns were degraded: intensity modulation along the streaks increased and the original reconstruction in the [110] and [$1\bar{1}0$] azimuths was lost as shown in Fig. 1c and d. Quadrupole mass spectrometry of the residual gases in the growth chamber indicated large quantities of Zn and S_2 were present, probably caused by evaporation from the radiantly-heated ZnS furnace shutter. Consequently, it appears that there was some exposure of the GaAs surface to Zn and/or S_2 before molecular beam impingement.

The structure of the GaAs (001) surface after intentional exposure to the Zn/S_2 flux was studied as part of the high temperature nucleation procedure for ZnS layer growth. The substrate temperature was 520°C with a beam equivalent pressure of 1.7 x 10^{-6} torr of both Zn and S_2 impinging on the surface. The associated RHEED patterns are shown in Fig. 2. Examination of the diffraction patterns in both the [110] and [$1\bar{1}0$] azimuths show spots due to transmission diffraction. Streaks connecting the transmission diffraction spots with a faint 4-fold reconstruction along the streaks were also visible in the [110] azimuth. These streaks are attributed to electron diffraction from ZnS surface facets comprised of both ($\bar{1}11$) and ($1\bar{1}1$) planes [20].

The RHEED patterns of Fig. 2 remained unchanged as long as the Zn/S_2 flux remained on the surface. When the flux was removed, the 2-fold reconstruction of Fig. 1c returned. The time for this change depended on substrate temperature while the detailed appearance of the patterns depended on the Zn/S_2 flux intensity. At 520°C the change occurred in 3 minutes while at 580°C the change was almost instantaneous. For small beam equivalent pressure (5 x 10^{-7} torr) at 580°C, the RHEED patterns remained unchanged from Fig. 1c and d. For larger fluxes the patterns of Fig. 2 developed but with decreased streak width and loss of the 4-fold reconstruction.

The 2-fold reconstruction in the [110] azimuth for GaAs prepared in poor vacuum conditions (ZnS furnace at 1100^{o}C) or under small Zn/S_2 fluxes is attributed to the surface chemisorption of sulfur since the GaAs surface is expected to be arsenic deficient after oxide desorption without an impinging As_4 flux. The sulfur dimer dissociates and bonds to surface gallium atoms which have unsatisfied bonds due to the loss of arsenic. Thus, the pattern of Fig. 1c and d corresponds to the surface $GaAs_xS_y$ layer postulated earlier. This identification is supported by Massies et al. low energy electron diffraction (LEED) observation of a (2x1) reconstruction on a GaAs (001) surface saturated with sulfur from H_2S [12]. For larger Zn/S_2 fluxes facetted ZnS island growth occurred, causing the transmission diffraction seen in the RHEED patterns of Fig. 2. However, at these temperatures (>500^{o}C) the ZnS islands will evaporate from the surface in the absence of an overpressure of Zn/S_2 flux, leaving the original $GaAs_xS_y$ surface layer. Therefore, for given Zn/S_2 flux and high substrate temperature, a steady state coverage of ZnS islands is present on the GaAs surface. The island coverage is constant when the rate of evaporation of ZnS from the island approximately equals the growth rate for the islands. The high evaporation rate of ZnS at these temperatures, ~1400 nm/hr. at 600^{o}C, supports this hypothesis [5].

After exposure of the GaAs surface to the Zn/S_2 flux at the oxide desorption temperature, the high temperature nucleation procedure continued with the substrate cooled under the Zn/S_2 to 175^{o}C. Negligible change (Fig. 2) occurred in the RHEED patterns until 470^{o}C, at which time surface modification was observed. In the [110] azimuth of Fig. 2a the 4-fold reconstruction was not observed; and large, diffuse transmission diffraction spots connected by streaks with a highly diffuse background developed for Zn/S_2 flux intensities between 5 x 10^{-7} torr and 2 x 10^{-6} torr. In addition, removal of the flux did not cause the RHEED pattern to revert to that shown in Fig. 1c and d: the evaporation rate of ZnS decreased sufficiently at these lower temperaturres to allow the ZnS islands to remain unperturbed on the surface. No change was observed along the $[1\bar{1}0]$ azimuth as the substrate temperature was lowered to 480°C.

As the substrate was further cooled to 175°C with Zn/S_2 incident, RHEED pattern quality improved due to surface smoothing with increasing ZnS layer thickness. After 5 minutes of growth at 175°C at a beam equivalent pressure of 5.6×10^{-7} torr, the transmission diffraction spots in the [110] and $[1\bar{1}0]$ azimuths elongated into streaks perpendicular to the shadow edge. The streaks connecting the transmission diffraction spots in the [110] azimuth also weakened dramatically, indicating island coalescense and a resultant reduction in electron diffraction from $(\bar{1}11)$ and $(1\bar{1}1)$ facet planes.

ZnS layers of thicknesses greater than 0.4μm grown using high temperature nucleation exhibited diffraction characteristic of smooth surfaces, although the detailed appearance depended on the initial roughness of the GaAs surface after oxide desorption. Figure 3a and b shows RHEED patterns from a ZnS layer grown on a GaAs substrate with average surface roughness. Intensity modulation along the streaks are present. The quality of the ZnS surface improved significantly with a smoother GaAs surface as shown in Fig. 3c and d. The RHEED patterns have less no intensity modulation along the streaks and a 2-fold reconstruction is present in the [110] azimuth, a feature not resolved from layers grown on rough GaAs surfaces.

Growth using low temperature nucleation proceeded qualitatively the same as in high temperature nucleation. ZnS islands grew with (111)-type facets and coalesced with continued growth to give smoother surfaces. However, in comparison to high temperature nucleation, the ZnS layers were rougher when nucleated at low temperatures. Unfortunately, these results were obscured by variations in the quality of the GaAs nucleation surface as illustrated earlier. In addition, sulfur and zinc present in the residual vacuum sometimes adsorbed on the GaAs surface during cooling causing premature ZnS nucleation. Thus, high temperature nucleation proved superior to low temperature nucleation for the production of smooth ZnS epitaxial layers.

3.2 Structural Characterization

X-ray structural characterization consisted of double crystal rocking curve and substrate-layer misorientation measurements. A definite relationship between the full width at half maximum (FWHM) of the rocking curves and layer thickness existed, although the nucleation procedure did not significantly affect the layer quality as accessed by DCRC (Fig. 4). The decrease in FWHM with thickness is typical of MBE heterostructure samples [21]. The FWHM for layers over 1.5μm are equal to or less than values reported in the literature for ZnS layers on GaAs [5-8].One group of specimens, grown on rougher substrates, had somewhat worse FWHM; these are indicated in Fig. 4 by the solid symbols. Thus, FWHM measurements showed that higher quality material was obtained for growth on smoother GaAs surfaces.

The variation in FWHM as a function of ϕ was generally between 200 and 300 arc seconds. For specimens 8, 17, 18, 21 and 24 the lowest FWHM were observed when $<110>_{ZnS}$ was parallel to the plane of the diffractometer ($\phi = 0^o$). Specimens 19, 25, 26 and 27 had minimum FWHM when other directions were in this plane. This partition of specimens was consistent with the grouping described in the previous paragraph: a well-defined curve of FWHM vs. layer thickness for samples 8, 10, 11, 12, 15, 17, 18, 21 and 24 and a second group of higher FWHM for the other specimens. Layer-substrate misorientation angles were measured for a number of specimens and varied from 0.1^o and 0.3^o. There was poor correlation between the misorientation angles and layer thickness, FWHM, or the nucleation technique.

Rocking curves were also measured as a function of position on the crystal using a $1mm^2$ square x-ray beam. Specimen 24, for example, had the following values of FWHM for positions separated by 3mm translation steps: 1254, 1167, 1244 and 1420 seconds. The larger value was probably due to handling and/or cleavage damage near the edge of the crystal. Rocking curves obtained with the asymmetric [113] and [$\bar{1}\bar{1}$3] diffraction vectors showed FWHM values which were quite similar to those obtained with [004]. For sample 24 (0.8 μm ZnS thickness) FWHM was 1030 and 1020 for h= [113] and [004], respectively. For sample 19 (2.1 μm thickness) FWHM was 655, 645 and 740 for h=[113], [$\bar{1}\bar{1}$3] and

[004], respectively. These sample thicknesses and asymmetry angles were not sufficient to remove completely the contribution from the ZnS/GaAs interface region. The sample 19 results, however, indicated that the uppermost ZnS material was of considerably better quality than that obtained in the interface region.

4. CONCLUSIONS

ZnS epitaxial layers were grown by MBE on GaAs (001) substrates using both low and high temperature nucleation techniques. RHEED analysis of layers grown using both techniques indicates that high temperature nucleation gave smoother ZnS surfaces, although the DCRC results were insensitive to the nucleation temperature. The quality of the ZnS layers as accessed by RHEED and DCRC critically depended on the initial roughness of the GaAs surface.

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FIGURE CAPTIONS

Fig. 1 RHEED patterns of GaAs surface after oxide desorption in different vacuum conditions. Clean residual vacuum: (a) [110] and (b) [110] azimuths. Residual vacuum with sulfur and zinc present: (c) [110] and (d) [110] azimuths.

Fig. 2 RHEED patterns of GaAs surface at 520^{o}C with Zn/S_2 molecular beam incident on surface. (a) [110] and (b) [110] azimuths.

Fig. 3 RHEED patterns of ZnS epitaxial layer grown using high temperature nucleation. Layer grown on rough GaAs surface: (a) [110] and (b) [110] azimuths. Layer grown on smoother GaAs surface: (c) [110] and (d) [110] azimuths.

Fig. 4 Variation in ZnS FWHM with epitaxial layer thickness. Circles represent layers grown using high temperature nucleation; squares represent layers grown using low temperature nucleation. Solid symbols are layers grown on GaAs substrates with poor surface smoothness.

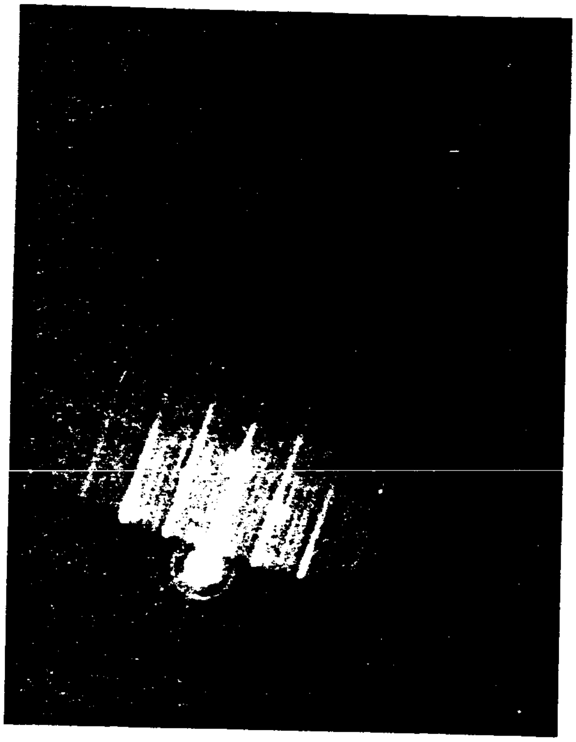

Fig 1a

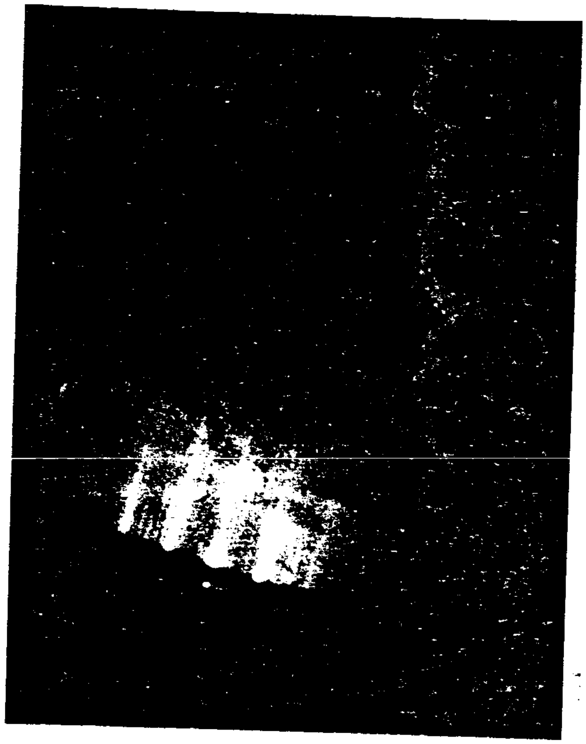

Fig. 1b

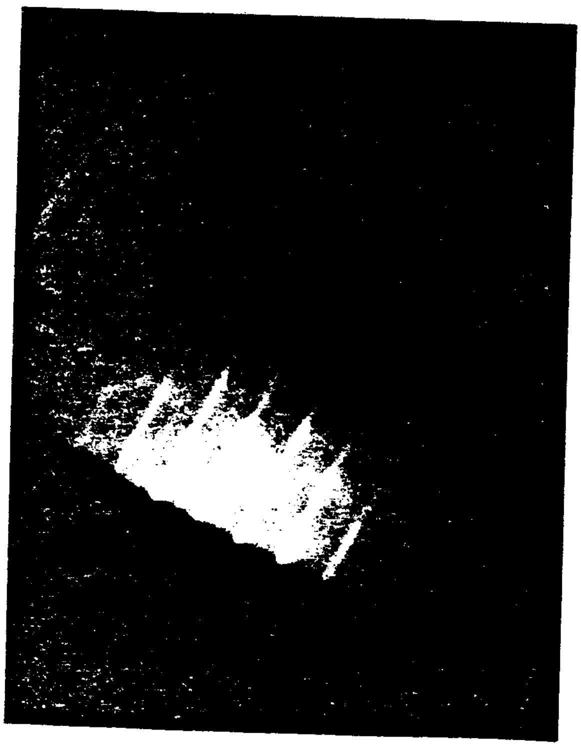

Fig 1c

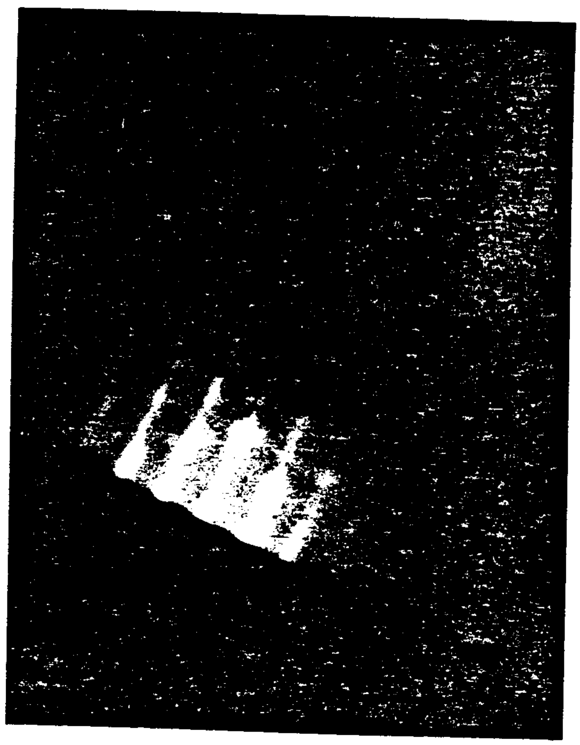

Fig. 1d

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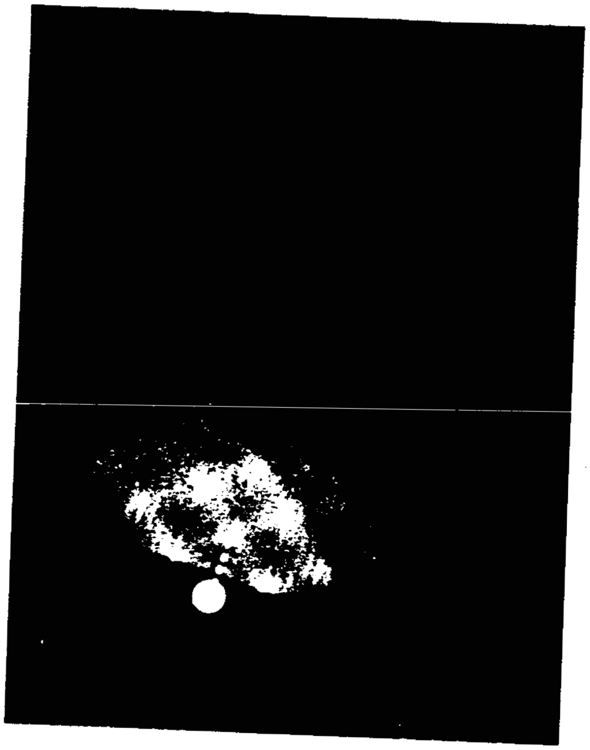

Fig 2a

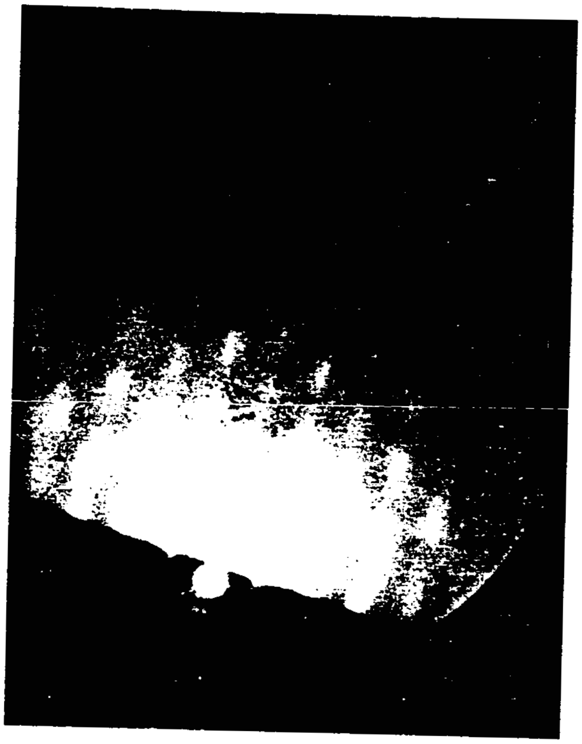

Fig 2b

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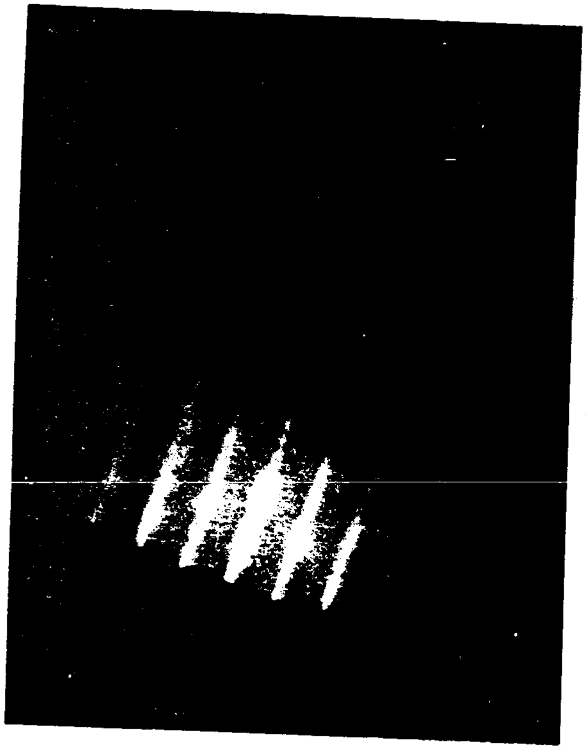

Fig 3a

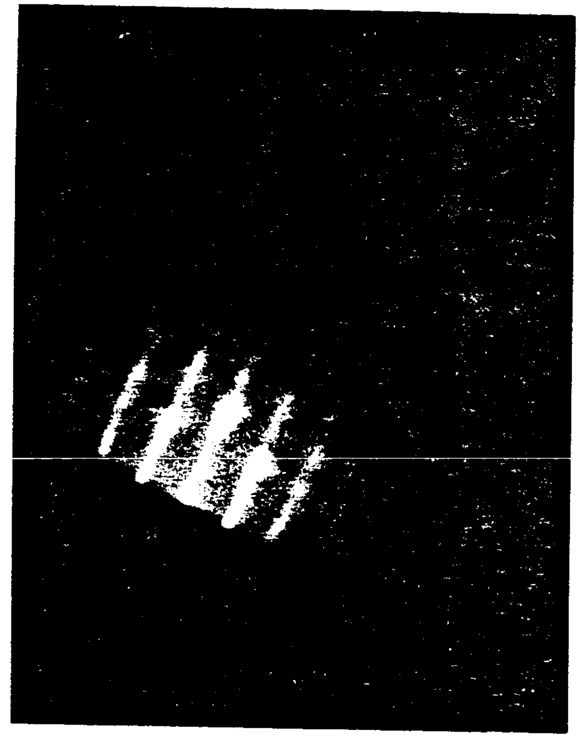

Fig.3 b

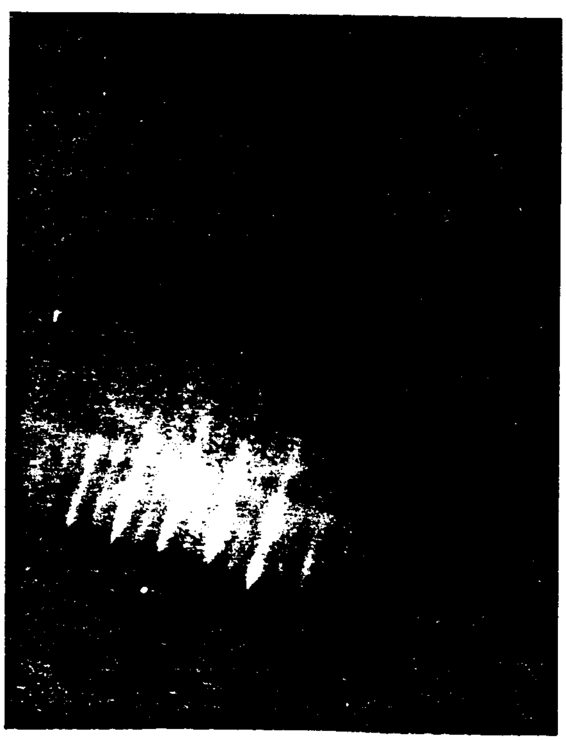

Fig.3c

Fig.3d

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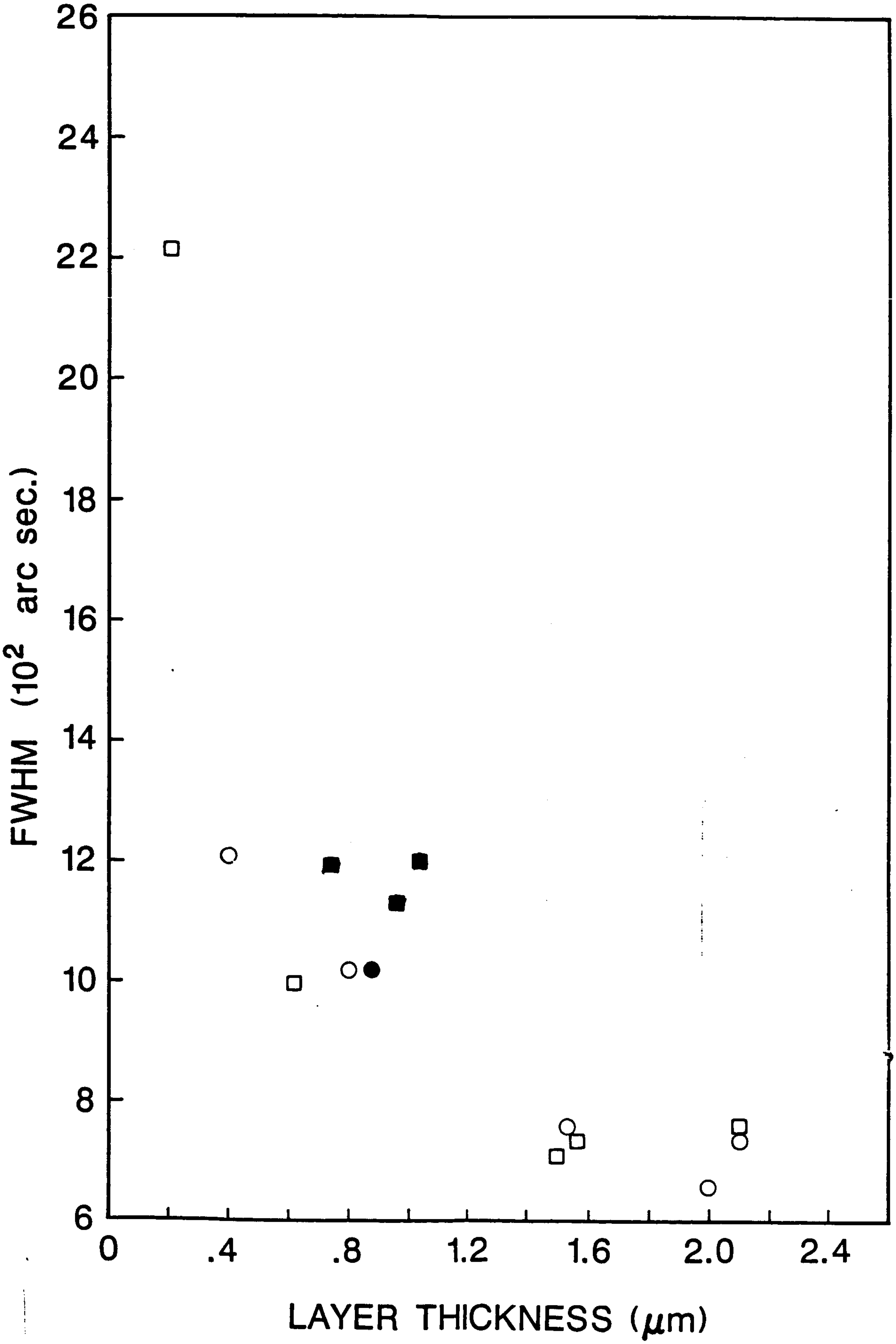

Fig. 4
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